

PCT

WORLD INTELLECTUAL PROPE
International Bu

INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9606916A1

(51) International Patent Classification ⁶: C11D 11/00, 1/02, 1/14	A1	(11) International Publication Number: WO 96/06916 (43) International Publication Date: 7 March 1996 (07.03.96)
(21) International Application Number: PCT/EP95/03321 (22) International Filing Date: 19 August 1995 (19.08.95) (30) Priority Data: 9417356.4 26 August 1994 (26.08.94) GB (71) Applicant (for AU BB CA GB IE KE LK MN MW NZ SD SG SZ TT UG only): UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE KE LK MN MW NZ SD SG SZ TT UG): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors: EMERY, William, Derek; West Garth, 64 Plymyard Avenue, Bromborough, Wirral, Merseyside L62 6BP (GB). METCALFE, Kenneth; 29 Antons Road, Pensby, Wirral, Merseyside L61 9PT (GB). TOLLINGTON, Peter, James; 16 Grange Mount, Heswall, Wirral, Merseyside L60 7TB (GB). (74) Agent: GEARY, Stephen; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PRODUCTION OF ANIONIC SURFACTANT GRANULES		
(57) Abstract A process for producing granules of anionic surfactant, preferably PAS by heating an aqueous paste of the surfactant to a temperature in excess of 130 °C and subsequently cooling the feedstock to provide surfactant granules, detergent particles obtainable by the process and compositions containing them are disclosed.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PRODUCTION OF ANIONIC SURFACTANT GRANULES

5 The present invention relates to detergent particles, a process for their production and a composition containing them. More particularly the present invention relates to a process for the production of detergent particles having a high level of anionic surfactant which involves drying a detergent paste containing the anionic surfactant and to the particles thereby obtained.

10 Detergent-active compounds conventionally employed in detergent compositions include anionic surfactants e.g. linear alkylbenzene sulphonates (LAS), linear alkyl ether sulphate (LES) and primary alkyl sulphates (PAS), and
15 nonionic surfactants e.g. alcohol ethoxylates. To improve detergency performance it is desirable to provide a high level of detergent-active material in the powder.

20 Often, the maximum level of active that may be incorporated is limited by process requirements. Detergent compositions having a high bulk density are typically prepared by a process involving mixing or granulation of components of the composition and/or a base powder obtained for example from a spray-drying process and provide significant consumer
25 benefits as compared to compositions of lower bulk density. It is known to incorporate detergent active compounds into such compositions in liquid form. However as it is necessary to control the ratio of liquids to solids in order to form detergent granules the maximum level of detergent active
30 material which may be incorporated in this manner is limited. It is also known to incorporate anionic surfactant e.g. PAS in detergent compositions by means of a solid adjunct, that is, a particle comprising the surfactant and other components of the composition e.g. sodium carbonate and builder.
35 Hitherto, the level of anionic surfactant present in such

- 2 -

adjuncts has been limited due to the need to provide good flow properties and reduce the tendency to agglomerate.

5 EP-A-506 184 (Unilever) discloses a process for the continuous dry neutralisation of liquid acid precursor of anionic surfactant. Detergent particles having an active detergent content of 30 to 40% by weight may be prepared by this process.

10 EP 572 957 discloses a process for producing a powdery anionic surfactant by feeding an aqueous slurry of the surfactant containing 60 to 80% solids into an evaporator, forming a film of the surfactant on the reactor wall and scraping it from the wall whilst drying and concentrating the
15 slurry.

It is disclosed that the reactor wall is at a temperature of 50 to 140°C; 130°C is the highest wall temperature exemplified. Higher temperatures are said to cause thermal
20 degradation and colour tone change and are thus disadvantageous. Further, EP 572 957 discloses that the blades in the reactor are operated to provide a tip speed of preferably 2 to 20 m/s, with 10.5 m/s being the highest tip speed which is exemplified. Bulk densities of up to about
25 0.5 g/cm³ are disclosed.

We have found that contrary to the teaching of the prior art detergent particles having a high bulk density, a high level of anionic surfactant and excellent powder properties may be
30 produced by heating a paste containing the surfactant in a first zone at a higher temperature than hitherto envisaged in the art and then cooling the thus formed particles. Moreover process throughput may be increased and the level of fine material and the particle size distribution of the particles
35 may be carefully controlled.

- 3 -

Accordingly a first aspect of the invention provides a process for the production of detergent particles comprising at least 75%, preferably at least 85% by weight of an anionic surfactant and no more than 10% by weight of water which
5 comprises feeding a paste material comprising water in an amount of more than 10% by weight of the paste and the surfactant into a drying zone, heating the paste material to a temperature in excess of 130°C and preferably in excess of 140°C in the said drying zone to reduce the water content to
10 not more than 10% by weight and subsequently cooling the material to form detergent particles wherein at least 80% of the particles have a particle size of 180 to 1500 µm and less than 10% have a particle size less than 180 µm.

15 Desirably the drying zone is under a slight vacuum to facilitate the removal of water and volatiles. The vacuum may be from 100 Torr up to atmospheric pressure as this provides significant process flexibility. However, a vacuum in excess of 500 Torr up to atmospheric has the advantage of
20 reducing capital investment whilst providing vacuum operation.

We have found that improved control of residence time and particle size may be secured and process throughput may be
25 increased by agitating the material in the drying and/or cooling zone.

A second aspect of the invention provides a process for the production of detergent particles comprising at least 75% and
30 preferably at least 85% by weight of an anionic surfactant and no more than 10% by weight of water which comprises feeding a paste material comprising water in an amount of more than 10% by weight of the paste and the surfactant into a drying zone, heating the paste to a temperature in excess
35 of 130°C and preferably in excess of 140°C and agitating the

- 4 -

paste with agitation means which have a tip speed in excess of 15 ms^{-1} and preferably in excess of 20 ms^{-1} to reduce the water content to not more than 10% by weight and subsequently cooling the material to form detergent particles wherein at least 80% of the particles have a particle size of 180 to 1500 μm and less than 10% have a particle size less than 180 μm .

The process is preferably continuous as this facilitates continuous transportation of the particles. In a continuous process the flow rate is suitably of the order of 10 to 25 $\text{kg/m}^2/\text{hr}$ and preferably 17 to 22 $\text{kg/m}^2/\text{hr}$ e.g. 20 $\text{kg/m}^2/\text{hr}$.

Suitably the average residence time in the drying zone is less than 5 minutes. A residence time of less than 4 minutes is especially preferred with as low a residence time as possible being most preferred.

Agitation of the paste in the heating zone generally provides efficient heat transfer within the paste and facilitate removal of water. Agitation reduces the contact time between the paste particles and the wall of the drying zone which, together with efficient heat transfer, reduces the likelihood of 'hot spots' forming which may lead to decomposition. Moreover, improved drying is secured thus allowing a shorter residence time/increased throughput in the drying zone.

To avoid thermal decomposition, the paste material is preferably not heated to a temperature in excess of 170°C .

The process of the present invention permits the formation of particles having a high bulk density for example in excess of 550 g/cm^3 .

- 5 -

The material is cooled in a cooling zone which is suitably operated at a temperature not in excess of 50°C and preferably not in excess of 40°C e.g. 30°C. Desirably there is agitation within the cooling zone to provide efficient cooling of the material therein. By actively cooling the particles, the possibility of thermal decomposition occurring due to the particles being heated to a higher temperature than previously disclosed, is reduced and the tackiness of the particles may be reduced. Such active cooling may be through circulation of, for example, cold water or liquid nitrogen around the cooling zone, for example, in a cooling jacket.

The paste material preferably comprises a mixture of anionic surfactant and water although other components may be present if desired or carried through as impurities from an up-stream process, for example production of the surfactant.

Preferably the paste material comprises at least 60% by weight, more preferably at least 65% and especially at least 70% by weight of anionic surfactant. Suitably the paste comprises no more than 40% and preferably no more than 30% by weight of water. The paste material should be pumpable at the temperature at which it is to be fed into the drying zone and this may limit the maximum level of surfactant present therein.

The paste is suitably fed to the drying zone at a temperature of 50 to 70°C and preferably 50 to 65°C where the paste comprises PAS, LES and/or LAS.

The process of the invention may be carried out in any suitable apparatus however it is preferred that a flash reactor is employed. Suitable flash reactors include e.g. the Flash Drier system available from VRVSpA processi Impianti Industriali. Desirably drying zone has a heat transfer area

- 6 -

of at least 10m^2 . The cooling zone desirably has a heat transfer area of at least 5m^2 .

5 Optionally two or more drying zones may be employed before the cooling zone as desired. A single apparatus may be employed to provide the drying zone and cooling zone as desired or alternatively separate apparatus for example a drier and a cooling fluid bed may be employed.

10 Suitably the drying zone is substantially circular in cross section and is thus defined by a cylindrical wall. Preferably the said wall is heated by means of a heating jacket through which water, steam or oil may be fed. The inside of the said wall is preferably maintained at a
15 temperature of at least 130°C and especially at least 140°C . Preferably the drying zone has an evaporation rate of 3 to 25, and especially 5 to 20 kg water per m^2 of heat surface per hour.

20 The cooling zone is preferably defined by a cylindrical wall. Where the process is continuous, the apparatus is suitably arranged such that the drying zone and cooling zone are substantially horizontally aligned to facilitate efficient drying, cooling and transport of the material through the
25 drying and cooling zones in a generally horizontal direction.

Suitably the drying zone and preferably the cooling zone have agitation means therein which agitates and transports the surfactant paste and forming granules through the said zones.
30 The agitation means preferably comprises a series of radially extending paddles and/or blades mounted on an axially mounted rotatable shaft. Desirably the paddles and/or blades are inclined in order to effect transportation and preferably have a clearance from the inner wall of no more than 10mm,
35 for example 5mm.

- 7 -

We have found that the present invention has especial applicability in the production of detergent particles comprising PAS. PAS is presently available on the market in fine powder form or in noodle form. The fine powder is generally dusty, having a significant quantity of particles of less than 150 microns. PAS noodles are generally produced by extruding dried PAS which has the appearance of soap chips and typically have a very large particle size and a very low porosity leading to poor dissolution characteristics. To increase the level of detergent active material in a detergent composition it is known to post-dose detergent particles to provide a composition having a high level of active material.

However, PAS in fine powder form and PAS noodles are generally not suitable for post-dosing into a detergent composition as the composition particles and the post-dosed particles are generally of different particle size and thus tend to segregate and be unsightly. The process according to the present invention enables detergent particles having a high level of detergent active material and suitable porosity and particle size characteristics to be obtained.

Accordingly a third aspect of the invention provides detergent particles comprising at least 60 % by weight of the particle of an anionic surfactant, preferably PAS, and not more than 10% by weight of the particle of water, the particles being obtainable by a process according to the first or second aspect of the invention.

According to a fourth aspect of the invention there is provided detergent particles comprising an anionic surfactant, preferably PAS and preferably in an amount of at least 60% by weight of the particle, wherein the particles have a porosity of 5 to 50% volume of the particle and a

particle size distribution such that at least 80% of the particles have a particle size of 180 to 1500 microns, preferably 250 to 1200 microns and less than 10% and preferably less than 5% of the particles have a particle size less than 180 μm .

Suitably the anionic surfactant in the detergent particles is present in an amount of at least 85% preferably at least 90% and desirably at least 94% by weight of the particles. It is desirable that the particles also comprise water in an amount of 1 to 10% and preferably 1 to 8% by weight of the particles. The water in the particle provides improved granule integrity thus reducing the level of the fine particles.

Suitably at least 80%, preferably 90% and more preferably 95% of the particles have a mean particle size of 300 to 1000 microns and more preferably 400 to 900 microns.

Desirably the detergent particles have an aspect ratio not in excess of 2 and more preferably are generally spherical in order to reduce segregation from other particles in a formulated detergent composition and to enhance the visual appearance of the powder.

Suitably the PAS surfactant has a chain length of C_{10} to C_{22} preferably C_{12} to C_{18} and more preferably a narrow range of C_{12} to C_{14} , Coco PAS is particularly desirable.

The detergent particle may comprise mixtures of PAS with other surfactants and/or non surfactant components as desired.

Suitable other surfactants may comprise alkyl benzene sulphonates, oxo alcohol sulphates for example C_{11} to C_{15} and

- 9 -

C₁₁ to C₁₅ alcohol sulphates, secondary alcohol sulphates and sulphonates, unsaturated surfactants for example sodium oleate, oleyl sulphates, α -olefin sulphonate, or mixtures thereof.

5

Especially preferred are PAS rich particles, that is particles in which the amount of PAS exceeds the amount of any other surfactant or non-surfactant and more preferably exceeds the total amount of all other surfactant and non-surfactant components.

10

Generally the sodium salt of the surfactants will be employed.

15

In general, PAS active has poorer water-solubility characteristics than other commonly used detergent-actives, for example LAS. This is especially the case at lower water temperatures which are typically employed for fabric washing in some countries. The dissolution characteristics for detergent particles comprising PAS and especially PAS-rich particles are influenced by such characteristics. It is desired to improve the solubility thereof especially in cold waters to reduce problems of deposition of the undissolved material on washed fabrics and wash inefficiency through non-participation of some particles in the washing process.

20

25

We have found that the dissolution characteristics of particles comprising PAS may be improved by reducing the Krafft temperature of the PAS active to below 13°C, the Krafft temperature for PAS which is conventionally employed in detergent products.

30

Accordingly, a further aspect of the invention provides detergent particles comprising PAS, preferably at a level of at least 60%, more preferably at least 70% and especially at

35

- 10 -

least 85% by weight of the particle, wherein the PAS has a Krafft temperature below 13°C and the average particle size is from 180 to 1500 µm.

5 Preferably the particles are produced by a process according to the invention as herein described.

Suitably at least 50% and especially at least 70% of the PAS has a linear alkyl chain.

10 Preferably the Krafft temperature is below 10°C and more preferably below 5°C as the solubility of the PAS is significantly superior at temperatures above the Krafft temperature.

15 The Krafft temperature of the PAS may be reduced by any suitable means.

20 It has been surprisingly found that by employing a narrow alkyl chain length distribution, the Krafft temperature thereof may be reduced. Preferably at least 90% and preferably at least 95% of the PAS active has a chain length of C₁₂ to C₁₆ and especially, for example EMPICOL LXV100 (tradename) ex Albright and Wilson.

25 The Krafft temperature may also be reduced by employing a branched detergent active, preferably an alkyl benzene sulphonate, alcohol sulphate, Guerbet alcohol sulphate, secondary alcohol sulphate, secondary alkyl sulphonates,
30 secondary and preferably premixing together with a linear alcohol sulphate. Branched chain surfactants may assist in foam generation which is desirable for the consumer in some markets.

- 11 -

Examples of suitable branched surfactants include PETRELAB 550, LIAL 123 AS (ex DAC).

5 The Krafft temperature of the PAS may be reduced by employing a quaternary ammonium counterion for up to 50 mole%, preferably up to 30 mole% and especially up to 20 mole% of the detergent active in particles. Preferably the quaternary ammonium counterion is selected from ammonium and quaternised mono, di or tri alkanol amine, for example ethanol amines.

10 Examples of suitable materials include the TEXAPON (tradename) range of surfactants ex Henkel.

15 The Krafft temperature may be lowered by employing, a narrow chain length distribution, a branched chain surfactant or a quaternary ammonium counterion, preferably a combination of these factors is employed to achieve further improvement in the solubility of the detergent particles.

20 Other non-surfactant components which may be present in the detergent particles include dispersion aids, preferably polymeric dispersion aids and more preferably urea, sugars, polyalkyleneoxides; and builders as hereinafter described.

25 If desired the detergent particles may comprise an organic and/or inorganic salt. Suitable materials in salts, preferably sodium, of tripolyphosphate, citrates, carbonates, sulphates, chlorides.

30 It is especially preferred that a salt be present in the particle when the anionic surfactant comprises LAS.

The salt may be present at a level of up to 40% and preferably up to 30% by weight of the particles.

35

- 12 -

The detergent particles may be post-dosed directly to a base powder obtained from any conventional detergent production process including a non tower process in which the components of the detergent composition are mixed and granulated as described e.g. in EP-A-367 339 (Unilever) and a spray drying process optionally followed by a post tower densification. As the detergent particles produced by the present invention may be post-dosed to such powders a significant degree of formulation flexibility is obtained and the level of active material in the fully formulated composition may be very high as desired. A further advantage is that a base powder which is substantially free of detergent active compounds may be produced as the detergent active compounds may be introduced substantially wholly as post-dosed particles.

Accordingly a further aspect of the invention provides a detergent composition comprising detergent particles according the third or fourth aspects of the invention and a base powder.

The option of reducing the level of detergent active material in a base powder is especially advantageous where the base powder is produced by a spray drying process as a lower level of detergent active compound in the spray drying process permits a higher throughput to be secured thus increasing overall production efficiency.

Compositions according to the fifth aspect of the invention generally contain, in addition to the detergent-active compound, a detergency builder and optionally bleaching components and other active ingredients to enhance performance and properties.

- 13 -

Detergent compositions of the invention may contain, in addition to the post-dosed detergent particles, one or more detergent-active compounds (surfactants) which may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C8-C15; primary and secondary alkyl sulphates, particularly C12-C15 primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulposuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

The total amount of surfactant present in the detergent composition is suitably from 5 to 40 wt% although amounts outside this range may be employed as desired.

- 14 -

The detergent compositions of the invention generally also contain a detergency builder. The total amount of detergency builder in the compositions is suitably from 10 to 80 wt%, preferably from 15 to 60 wt%. The builder may be present in an adjunct with other components or, if desired, separate builder particles containing one or more builder materials may be employed.

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate, may also be present, but on environmental grounds those are no longer preferred.

Zeolite builders may suitably be present in an amount of from 10 to 60 wt% and preferably an amount of from 15 to 50 wt%. The zeolite used in most commercial particulate detergent compositions is zeolite A. Advantageously, however, maximum aluminium zeolite P (zeolite MAP) described and claimed in EP 384 070A (Unilever) may be used. Zeolite MAP is an alkali metal aluminosilicate of the P type having a silicon to aluminium ratio not exceeding 1.33, preferably not exceeding 1.15, and more preferably not exceeding 1.07.

Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di-

- 15 -

and trisuccinates, carboxymethyloxysuccinates,
carboxymethyloxymalonates, dipicolinates,
hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and
succinates; and sulphonated fatty acid salts. A copolymer
5 of maleic acid, acrylic acid and vinyl acetate is especially
preferred as it is biodegradable and thus environmentally
desirable. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitably
10 used in amounts of from 5 to 30 wt%, preferably from 10 to 25
wt%; and acrylic polymers, more especially acrylic/maleic
copolymers, suitably used in amounts of from 0.5 to 15 wt%,
preferably from 1 to 10 wt%. The builder is preferably
present in alkali metal salt, especially sodium salt, form.

15 Suitably the builder system comprises a crystalline layered
silicate, for example, SKS-6 ex Hoechst, a zeolite, for
example, zeolite A and optionally an alkali metal citrate.

20 Detergent compositions according to the invention may also
contain a bleach system, desirably a peroxy bleach compound,
for example, an inorganic persalt or organic peroxyacid,
capable of yielding hydrogen peroxide in aqueous solution.
The peroxy bleach compound may be used in conjunction with a
25 bleach activator (bleach precursor) to improve bleaching
action at low wash temperatures. An especially preferred
bleach system comprises a peroxy bleach compound (preferably
sodium percarbonate optionally together with a bleach
activator), and a transition metal bleach catalyst as
30 described and claimed in EP 458 397A, EP 458 398A and
EP 509 787A (Unilever).

The compositions of the invention may contain alkali
metal, preferably sodium, carbonate, in order to increase
35 detergency and ease processing. Sodium carbonate may

- 16 -

suitably be present in an amount from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

5

Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate polymer, or sodium silicate which is

10 suitably present in an amount of from 1 to 5 wt%.

15

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; fluorescers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; foam controllers; and fabric softening compounds. This list is not intended to be

20 exhaustive.

25

The base composition is suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on, admixing and/or postdosing those ingredients unsuitable for processing via the slurry. The detergent particles produced according to the process of the present invention are post-dosed to the base composition by conventional methods.

30

Detergent compositions of the invention preferably have a bulk density of at least 500 g/l, more preferably at least 550 g/litre, more preferably at least 700 g/litre.

- 17 -

Such powders may be prepared either by spray-drying, by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation. A high-speed mixer/granulator may advantageously be used for such mixing. Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

The invention is illustrated by the following non-limiting Examples.

Example 1

An aqueous paste comprising 70% by weight of sodium cocOPAS was fed into the drying zone of a Flash Drier manufactured by VRVSpA, Italy at a temperature of 60°C. A small vacuum was applied to the drying zone. The initial throughput in the Flash Drier was 120 kg/hr of paste. The temperature of the wall of the drying zone was initially 140°C. The heat transfer area of the drying and cooling zones was respectively 10m² and 5m².

The temperature of the wall of the drying zone was raised in steps to 170°C. Correspondingly the throughput was increased to 430 kg/hr at 170°C. At each step the process conditions were stabilised for 15 minutes. The particles then passed to a cooling zone operated at a temperature of 30°C.

PAS granules comprising at least 85% PAS and 5 to 8.5% moisture content were obtained from each step having a bulk density of at least 550 g/l with a dynamic flow rate of at least 100 ml/s. The samples obtained all had a whiteness of at least 80 on a grey-scale of 1 (black) to 100 (white) measured using a Minolta CR-310 Chromameter. Commercially available detergent powders generally have a whiteness of at least 75 thus illustrating that little thermal decomposition leading to colour impairment had occurred.

The samples all contained less than 5% fine material (180 μm or less) and the particles exhibited good strength and low friability.

The solubility of the samples was tested in water at 20°C, conductivity being employed to measure the % dissolution. In all cases, at least 75% of the sample had dissolved after 20 seconds and at least 95% after 30 seconds illustrating the excellent solubility characteristics of the PAS granules.

20

Example 2

The procedure of Example 1 was repeated using a small scale Flash Drier having a heat transfer surface area of 0.5m² (drying area: cooling area =2:1). The agitator tip speed was about 30ms⁻¹ and the drying and cooling zones were operated at temperatures of 160°C and 40°C respectively. PAS granules containing 96 to 97.5% PAS and 1.5 to 2% moisture were obtained.

30

Example 3

An example of a detergent composition according to the invention is listed below in which the base powder, PAS granules and other components are dry-mixed:

35

- 19 -

Base Powder		60%
- Nonionic surfactant	12	
- Soap	2	
- Zeolite builder	38	
- Moisture, salts, NDOM	8	
PAS granules		9%
Percarbonate		20%
Minors (include foam suppressor, TAED, enzyme)		11%

The composition exhibited good detergency and dissolution characteristics.

Example 4

A series of compositions containing LAS as the detergent actives were produced as detailed in the following Table, by the procedure outlined below.

	Product Composition as Weight %				
LAS	75	77.0	79.5	75.6	68.2
Water	2.0	2.0	2.0	2.0	2.0
Sodium Citrate	0.0	0.0	8.9	18.9	0.0
STP	20	17.6	6.3	0.0	26.8
NDOM and minors	3.0	3.4	3.3	3.5	3.0

An aqueous paste of the components of the compositions was fed into the drying zone of a flash-drier having a heat transfer surface of 1.2m² (drying area:cooling area 2:1).

- 20 -

The agitated tip speed was about a 30ms^{-1} and the drying and cooling zones were operated at temperatures of about 160°C and 20°C respectively. The pastes were fed into the dryer at a feed rate of 10 to 30 kg hr^{-1} .

5

Solid particles containing LAS and a salt were produced satisfactorily.

Example 5 to 11

10

Examples of detergent particles according to the present invention and which may be produced by a process according to the present invention are listed in the following Table.

15 The time for 90% of the particles to dissolve in water at 5°C was measured using an AGB-4001 conductivity meter with a final surfactant concentration of 0.2 gl^{-1} in demineralised water.

20

	5	6	7	8	9	10	11
Coco PAS C_{12-14} sodium salt	100	50	80	70	80	90	76
^a TEA salt	-	-	-	10	20	10	-
^b LIAL 123 AS	-	50	20	20	-	-	19
^c PEG 4000	-	-	-	-	-	-	5
Dissolution time (mins)	20	1	3	1	0.5	1	3

25

^a triethanolamine

30

^b branched PAS sodium salt ex DAC

^c ex BDH

Claims

1. A process for the production of detergent particles comprising at least 75%, by weight of an anionic surfactant and no more than 10% by weight of water which comprises feeding a paste material comprising water in an amount of more than 10% by weight of the paste and the surfactant into a drying zone, heating the paste material to a temperature in excess of 130°C in the said drying zone to reduce the water content to not more than 10% by weight and subsequently cooling the material to form detergent particles wherein at least 80% of the particles have a particle size of 180 to 1500 μm and less than 10% have a particle size less than 180 μm .
2. A process for the production of detergent particles comprising at least 75% by weight of an anionic surfactant and no more than 10% by weight of water which comprises feeding a paste material comprising water in an amount of more than 10% by weight of the paste and the surfactant into a drying zone, heating the paste to a temperature in excess of 130°C and agitating the paste with agitation means which have a tip speed in excess of 15 ms^{-1} to reduce the water content to not more than 10% by weight and subsequently cooling the material to form detergent particles wherein at least 80% of the particles have a particle size of 180 to 1500 μm and less than 10% have a particle size less than 180 μm .
3. A process according to claim 1 or 2 in which the anionic surfactant comprises primary alkyl sulphate.
4. A process according to any preceding claim wherein the anionic surfactant is present in the particles at a level of at least 90% by weight of the particles.

- 22 -

5. Detergent particles comprising at least 60 % by weight of the particle of an anionic surfactant, and not more than 10% by weight of the particle of water, the particles being obtainable by a process according to the process according to claim 1 or 2.
6. Detergent particles comprising PAS wherein the PAS has a Krafft temperature below 13°C and preferably below 10°C.
7. Detergent particles according to claim 6 wherein the PAS has an alkyl chain length of C₁₂ to C₁₆.
8. Detergent particles according to claim 6 or 7 which further comprise a branched chain anionic surfactant.
9. Detergent particles according to claims 6 to 8 wherein the counterion of up to 50 mole% of the PAS is a quaternary ammonium ion.
10. Detergent particles according to any one of claims 5 to 9 wherein the particles have a porosity of 5 to 50% volume of the particle and a particle size distribution such that at least 80% of the particles have a particle size of 180 to 1500 microns, and less than 10% of the particles have a particle size less than 180 µm.
11. A detergent composition comprising detergent particles as defined in any one of claims 5 to 10 and a base powder comprising a surfactant and/or a builder and, optionally, further comprises an alkali metal percarbonate.
12. A detergent composition according to claim 11 in which the base powder comprises a builder comprising a

- 23 -

silicate, preferably a crystalline layered silicate,
and/or a zeolite.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 95/03321

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D11/00 C11D1/02 C11D1/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 572 957 (KAO CORP) 8 December 1993 cited in the application see page 3, line 47 - page 4, line 33; claims 1-5; example 4; table 1 ---	1-3,7, 11,12
A	EP,A,0 384 480 (KAO CORP) 29 August 1990 see claims; examples; table 1 ---	1,3,7, 11,12
A	WO,A,93 19155 (HENKEL KGAA) 30 September 1993 see claims; example 2 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 January 1996

Date of mailing of the international search report

30. 01. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax. (+ 31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 95/03321

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0572957	08-12-93	NONE	
EP-A-0384480	29-08-90	JP-A- 2222498 DE-T- 69001499 US-A- 5052122	05-09-90 28-10-93 01-10-91
WO-A-9319155	30-09-93	DE-A- 4209339 EP-A- 0632826 JP-T- 7504931	30-09-93 11-01-95 01-06-95

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.